The g-Factor of Ferromagnetic Spinels

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Synopsis

The ferromagnetic resonance in Ni–Zn and Mn–Zn binary ferrites and nickel ferrite aluminates have been studied as a function of composition at three wavelengths from 1 cm to 3.2 cm.

After studying the size effect of resonance phenomenon, apparent g-factor and line width were obtained at three frequencies as a function of composition. Then concerning the internal field in the specimen, the frequency independent g-factors were obtained from the data of three frequencies. It shows a monotonous decrease in Ni–Zn binary ferrites, while it remains constant in Mn–Zn binary ferrites, and shows interesting changes in nickel ferrite aluminates. These variation of g-factors with composition are well explained by the theory of ferrimagnetic resonance.

Investigations were also made into the relation between ferromagnetic resonance and the density of ferrite, and it was found that the porosity in the specimen play a major role in contributing to the frequency dependence of apparent g-factor.

I. Introduction

Many investigations have been made on the microwave ferromagnetic resonance in ferrites and many valuable informations on ferrites have been obtained from the resonance data. However, the reported values of certain ferrite are not in agreement with some experiments, especially for the value of spectroscopic splitting factor g, which is one of the most important factors in studying the ferromagnetism. We noticed the disagreement in the values of g-factor of ferrites, and studied from what origin these differences occurred.

After making investigations, we found that these disagreements were generally caused by the following reasons.

First, the size of specimen greatly affects the resonance phenomena. This was found first by Beljers and Polder,[1] and we also performed experiments on the effect and found that these effects more or less in almost all ferrites which were tested.[2] That is to say when the spherical specimen is used, the apparent g-factor changes with variations in its spherical diameter (generally it increases with decreasing diameter). In order to eliminate the size effect, resonance experiments should be performed on various specimens having different size, and the resonance field must be determined by extrapolating to zero size.

Second, the resonance phenomenon shows different appearance at different frequencies employed. For g-factor, even though determined by extrapolating to zero size, we could not obtain the same value at different frequencies for the same specimen.

(1) G.H. Beljers and D. Polder, Nature, **165** (1950), 800.

(2) T. Okamura and Y. Kojima, Phys. Rev., **86** (1952), 1040.

But as shown in our previous paper,[3] a simple relation has been found to exsist between the resonance field and the frequency employed, and from these facts we supposed that g-factor should be calculated by the relation

$$\nu = \frac{\gamma}{2\pi}(H_z + H_i), \qquad (1)$$

where H_z is the observed resonance field, H_i the internal field in the material and $\gamma = ge/2mc$. By using the equation (1), we could determine the g-factor of ferrite independent of frequency, and the reason for frequency dependence of apparent g-factor, which is calculated by Kittel's resonance condition[4]

$$\nu = \frac{\gamma}{2\pi}H_z, \qquad (2)$$

was found to lie in the negligence of the internal field.

Thus, in order to determine the g-value of ferrite, resonance experiments should be performed at different wavelengths, and frequency dependence of g-factor must be studied as well as the size effect at each frequency.

In the present paper, g-factor in the binary ferrites of Ni-Zn, Mn-Zn ferrites and nickel ferrite aluminates were determined by making use of the procedure described above. Moreover, several phenomena such as the change in half width or internal field with varying compositions are described and discussed.

Lastly, an investigation for the study of the origin of internal field was performed. For this purpose, the density of ferrite specimen was varied by treating it under various heating conditions, giving caution not to change the characteristic property of ferrite, and the relation between the resonance phenomenon and the effective density of the specimen was confirmed.

II. Experimental

The experimental method and procedure were the same as used in the usual resonance experiment and also shown in our previous paper,[5] so they are omitted here. The microwave frequencies employed in the present experiment were 9370 Mc, 19230 Mc and 28850 Mc. The oscillator used for the experiment at the longest wavelength was a klystron 723A/B, while for the experiments of 1.5 cm and 1 cm wavelength, the second and third harmonics were generated from the power of 723A/B by the crystal multiplier.

The spherical formed polycrystalline specimens, made by the pressing and sintering process, were used in all the experiments described below. Many specimens having various different diameters from about 0.3 mm to 3 mm were polished by Bond's method[6] from the ferrite block which was presintered at 1100°C for about one hour, then the small spheres were heat-treated at the temperature suitable to the object of each experiment, that is, at 1300°C for Ni-Zn binary ferrites, 1200°C for Mn-Zn

(3) T. Okamura, Y. Torizuka and Y. Kojima, Phys. Rev., **88** (1952), 1425.
(4) C. Kittel, Phys. Rev., **73** (1948), 155.
(5) T. Okamura, Y. Kojima and Y. Torizuka, Sci. Rep. RITU, **A4** (1952), 72.
(6) W.L. Bond, Rev. Sci. Inst., **22** (1951), 344.

binary ferrites, 1400°C for nickel ferrite aluminates, and at various temperature between 1200°C and 1400°C for the purpose of varying the density of the specimen, then spheres were slowly cooled to room temperature in the furnace. Then, resonance field and line width were observed on each specimen at three frequencies.

III. Results and discussions

Ni-Zn Ferrites

In order to study the resonance phenomena in relation to the composition variation in Ni-Zn binary ferrites, the experiments were performed on the specimens having various values of x in $Ni_{(1-x)}Zn_xFe_2O_4$ where x was varied from 0 to 1 at intervals of 0.1.

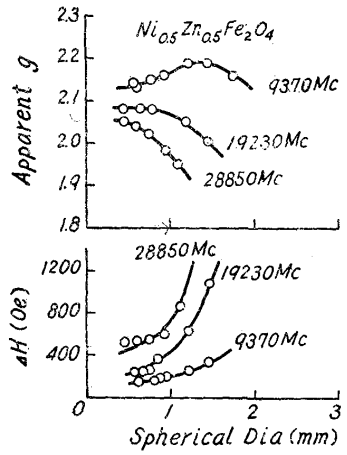

Fig. 1. Apparent g-factor and line width ΔH as spherical diameter of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at three frequencies showing the size effect.

Fig. 1 shows the curves of size effect for the apparent g-factor and line width ΔH in a certain composition of $Ni_{(1-x)}Zn_xFe_2O_4$, where the apparent g-factors were calculated by the equation (2) : the complicated curves of size effect for g-factor at 3.2 cm wavelength may be noticed in the figure, though cannot be explained quantitatively.

The apparent g-factor at each frequency was extrapolated to zero diameter and plotted as a function of the composition in Fig. 2: it shows a linear decrease with increasing x at longer wavelength and approaches a concaved curve at shorter wavelength. To eliminate the frequency dependence of g-factor, the resonance field at each frequency was inserted in the equation (1) and true g-values were calculated for each composition and plotted in Fig. 2 with closed circles.

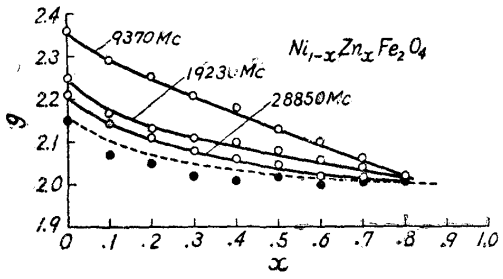

Fig. 2. g-factor of Ni-Zn binary ferrites as a function of composition.

Ferrimagnetic resonance has been treated theoretically by many physists, and g-factor of ferrimagnetics has been described by Tuya[7] and Wangsness[8] in respect to two sublattices as

$$g_{\text{eff}} = \frac{g_1 S_1 + g_2 S_2}{S_1 + S_2}, \qquad (3)$$

where, in the present experiment, g_1 and g_2 are g-factors of Ni^{2+} and Fe^{3+} and S_1, S_2 are spin angular momentums of Ni^{2+} and Fe^{3+}. Equation (3) should lead to a change in g-factor against the composition like the present results if we substitute the g-value of Ni^{2+} and its lattice distribution. In ferrimagnetics, the magnetic moment n_B per one molecule is represented as

(7) N. Tuya, Prog. Theoret. Phys., **7** (1952), 263.
(8) R. K. Wangsness, Phys. Rev., **91** (1954), 1085.

$$n_B = |(\sum_i x_i g_i S_i)_A - (\sum_i x_i g_i S_i)_B|, \qquad (4)$$

where x_i is the number of metalic ions on both sites per molecule, g_i is the g-factor of its ion and S_i is its total spin augular momentum.

For Ni ferrite, the measured value are $n_B = 2.2$ Bohr magnetons, and if a small fraction x of the Ni^{2+} ion is on a A site and $1-x$ is on a B site, equation (4) should be written as

$$2.2 = g_{Ni}(1 - 2x) + 10x,$$

while by substituting $g_{eff}=2.15$ in Ni ferrite according to the present result, equation (3) can be written as

$$2.15 = \frac{g_{Ni}(1-2x) + 10x}{1 + 3x}.$$

From the above relations we could obtain $g_{Ni} = 2.16$ and $x = 0.008$. Supposing the g-value of Ni^{2+} ion to be 2.16, the Ni^{2+} ion to be all on a B site and Zn^{2+} ion to be on a A site, g-value of Ni–Zn binary ferrites could be calculated from the relation of equation (3) as shown in Fig. 2 in a dotted line. It shows a good agreement with the present experiment within the experimental error of ±1%.

Fig. 3 shows H_i for each compsoition which was derived from the resonance fields at each frequency and used in determining the true g-factor of Ni-Zn binary ferrites. The curve does not signify the relation between H_i and composition, for H_i was found to have suffered serious effects from the porosity of specimen as described in a later section, and the specimens of various composition used in the present experiment have different porosity.

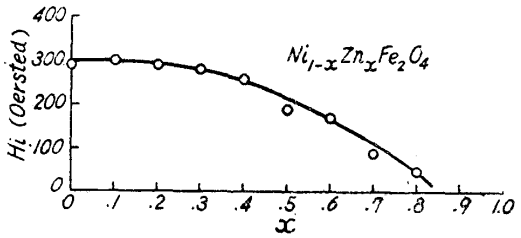

Fig. 3. H_i of Ni–Zn binary ferrites.

In Fig. 1, the size effect for line width ΔH shows different inclinaton for each frequency; a sufficient extrapolation to zero diameter is difficult, so it cannot be asserted experimentally whether the extrapolated value for each frequency exactly coincide with one another or not. As the curves for longer wavelength are rather to be extrapolated with ease, ΔH at 9370 Mc is plotted as a function of composition in Fig. 4.

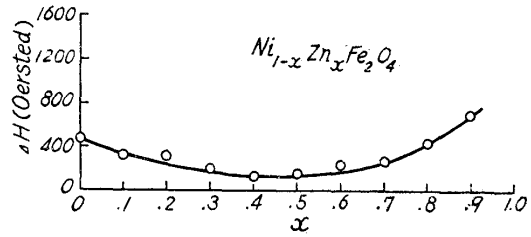

Fig. 4. Line width of Ni-Zn binary ferrites as a function of composition observed at 9370 Mc.

Width of the resonance line is mainly due to the magnetic anisotropy in ferrite when the polycrystalline specimen is used, and the value of ΔH may be given approximately by K/M. Though the value of ΔH in Fig. 4 shows the order of K/M, it takes a narrowest value near $x = 0.4$, which does not agree with the result of permeability measurement,[9] from which K/M has been found to be

(9) K. Ota, Private communication.

smallest near $x = 0.6$. The cause of line broadening found at high zinc ferrite concentration cannot be explained, but may be attributed to the decrease in exchange interaction by the addition of zinc ferrite.

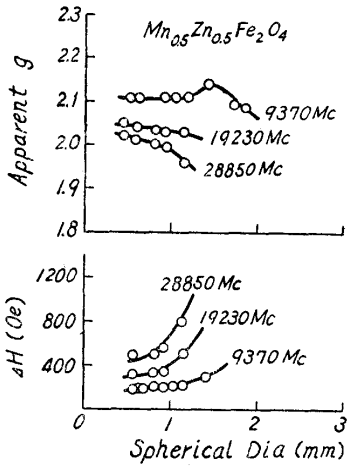

Fig. 5. Apparent g-factor and line width *vs* spherical diameter of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ at three frequencies showing the size effect.

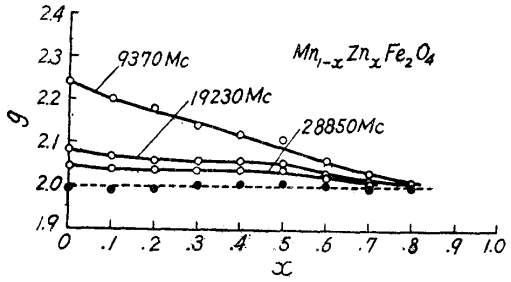

Fig. 6. g-factor of Mn-Zn binary ferrites as a function of composition.

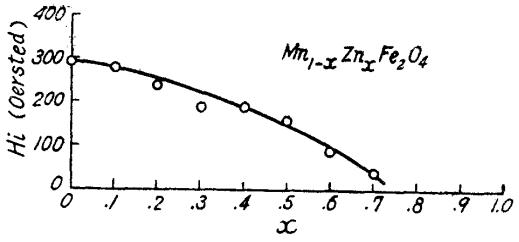

Fig. 7. H_i of Mn-Zn binary ferrites.

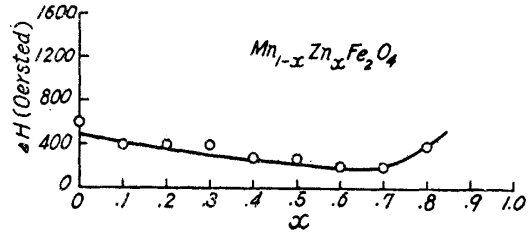

Fig. 8. Line width of Mn-Zn binary ferrites as a function of composition observed at 9370 Mc.

Mn-Zn Ferrites

The same experiments as those on Ni-Zn binary ferrites were also performed on Mn-Zn binary ferrites.

Fig. 5 shows the curves of size effect for apparent g-factor and line width ΔH at a certain composition of $Mn_{1-x}Zn_xFe_2O_4$. The apparent g-factor at each frequency was extrapolated to zero diameter and plotted as a function of composition in Fig. 6, and the true g-factor calculated from equation (1) was shown in the figure in closed circles.

As g-factor of Mn^{2+} and Fe^{3+} is 2, manganese ferrite and Mn-Zn ferrites should show the g-value to be 2, and this is in agreement with the present experiment as illustrated in Fig. 6. Fig. 7 shows H_i for each composition which was used in determining the true g-factor of Mn-Zn ferrites. It does not show the relation between H_i and composition as in the case of Ni-Zn binary ferrites because of various effective densities of each specimen. Fig. 8 shows the line width ΔH at 9370 Mc as a function of composition and it shows the narrowest value near $x = 0.6$.

Nickel ferrite aluminates

Resonance phenomena in nickel ferrite aluminates were also studied. The magnetic properties of nickel ferlite aluminates have been measured by McGuire,[10] Maxwell[11] and the others,[12] but they determined the g-factor, taking no notice

(10) T. R. McGuire, Phys. Rev., **93** (1954), 682.
(11) L. R. Maxwell and S.J. Pickart, Phys. Rev., **92** (1953), 1120.
(12) J. S. Smart, Phys. Rev., **94** (1954), 847.

of the internal field H_i.

The present experiments were carried out to determine the g-factor of $NiFe_{2-x}Al_xO_4$ according to the procedure described above in which x was varied in step of 0.2.

Fig. 9 shows saturation magnetization of $NiFe_{2-x}Al_xO_4$ as a function of x at room temperature measured in the field of 7500 Oe on cylindrical specimens. It suggests that in the region of $x<0.72$ and $x>0.72$ the origin of magnetization would be in 16c and 8f site respectively.

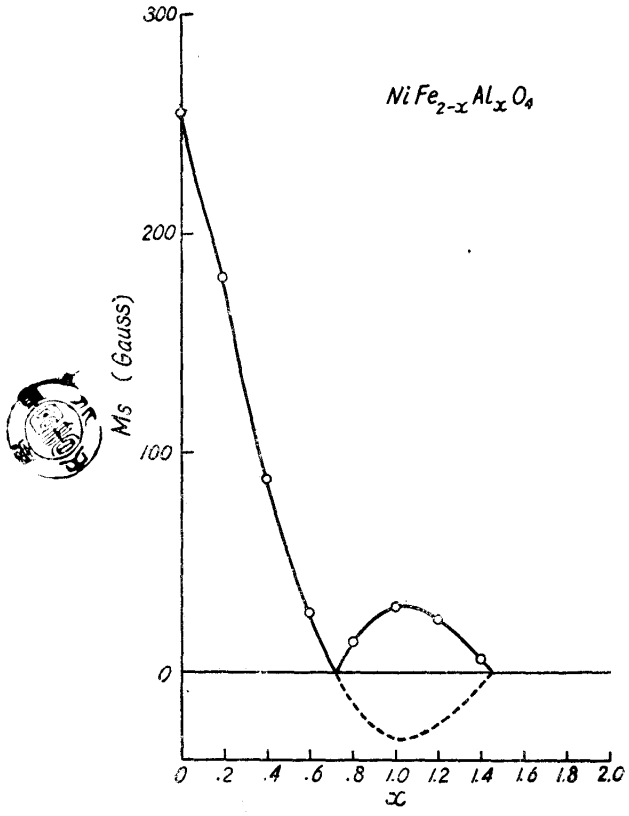

Fig. 9. Saturation magnetization of nickel ferrite aluminates as a function of composition.

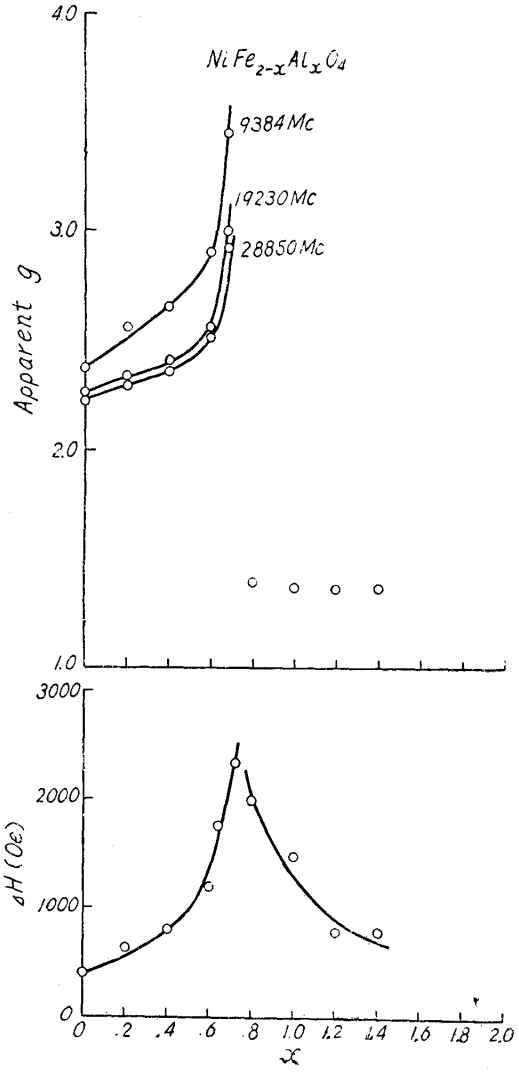

Fig. 10. Apparent g-factor and line width of nickel ferrite aluminates as a function of composition.

Fig. 10 gives an apparent g-factor of $NiFe_{2-x}Al_xO_4$ at three frequencies of 9384 Mc, 19230 Mc and 28850 Mc and the line width ΔH at 19230 Mc extraporated to zero diameter to eliminate the size effect. True g-value and H_i calculated from the equation (1) by using the results of 19230 Mc and 28850 mc are shown in Table 1. In the region of $x<0.72$, the change in g-factor with composition is well explained by the equation (3), but in the region of $x>0.72$ large discrepancies from the equation (3) are found,[13] although ΔH decreases with increasing x. From table 1, it is seen that the internal field H_i shows large values of 240~370 Oe in the region

(13) J. S. Smart reported that these g-values were explained by supposing the special g-value for Ni ion in tetrahedral site and taking the suitable cation distribution.

of $x < 0.72$, but the frequency dependence of g-factor was not found at $x > 0.72$. This would be noticed in a consideration of the origin of the internal field though not yet be explained theoretically.

Table 1. The true g-value and H_i of $NiFe_{2-x}Al_xO_4$ as a function of x.

x	0	0.2	0.4	0.6	0.68	0.8	1.0	1.2	1.4
g	2.16	2.20	2.29	2.45	2.80	1.40	1.37	1.37	1.37
H_i(Oe)	280	370	320	240	310	0	0	0	0

Mn and Ni ferrite of various densities

As described above, the frequency dependence of apparent g-factor which was calculated from Kittel's resonance condition of equation (2) can be explained well, if we consider the internal field of the specimen, and g-factor deduced from equation (1) with respect to the internal field seems to show a more accurate g-value. But the origin of this internal field has not yet been dissolved.

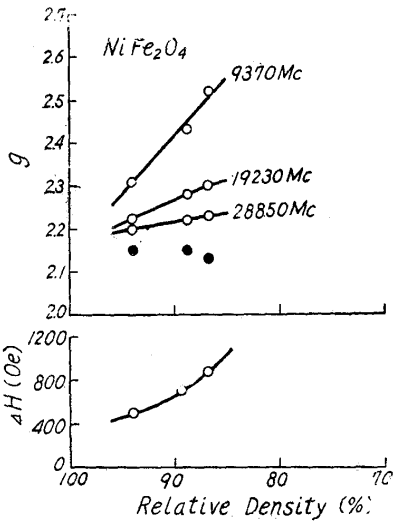

Fig. 11. g-factor and line width of nickel ferrite as a function of density.

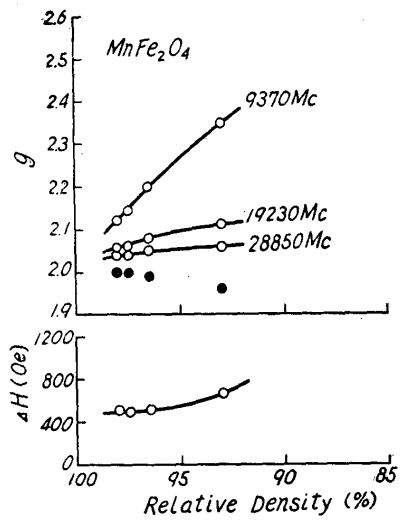

Fig. 12. g-factor and line width of manganese ferrite as a function of density.

Though the theoretical calculation of the origin of internal field concerning the effect of anisotropic field in the polycrystalline specimen or of relaxation process have been examined,[14] they have all given the negative result or have not been capable of explaining the existence of internal field which has the order of hundreds of oersteds in the case of nickel and manganese ferrite as described above. To ascertain the origin of internal field experimentally, we studied the relation between ferromagnetic resonance phenomena and the density of specimen. In polycrystalline ferrite, its effective density can be varied considerably without giving an excessive change in its magnetic property by various heat treatment.

Nickel ferrite and manganese ferrite chosen at present to perform the density experiment. They were heattreated at various temperatures from 1200°C to 1400°C for 3 hours and then slowly cooled in the furnace, preventing the occurrence of severe change in their property, i. e., treatment at temperature lower than 1200°C will result in an unsatisfactory reaction of raw material oxides, and at temperature higher than 1400°C, ferrite

(14) e. g. M. Date, Sci. Rep. RITU, **A 6** (1954), 109.

will resolve. The effective density of specimens treated in the above way was measured by observing their spherical diameter and their weight, while the true density was known from the X-ray data, the ratio of effective density to the X-ray density being calculated as the relative density of specimen. It was found that the relative density could be varied from about 87% to 94% in nickel ferrite and from 93% to 98% in manganese ferrite by heat treatment described above.

The size effect for apparent g-factor and line width was observed at three frequencies on the specimen of various densities. The extrapolated g-factor at each frequency and line width at 9370 Mc were plotted as a function of density in Fig. 11 and Fig. 12. The discrepancy of g-factor at each frequency decreased with increasing density, and the frequency dependence of apparent g-factor seem to become very small for the specimen of 100% density. Thus the porosity in the specimen was found to play a major role in contributing to the frequency dependence of apparent g-factor, but it is to be noticed that the true g-value calculated from the equation (1) is almost independent of density in the limit of experimental error except for the specimen of relatively low density as shown in closed circles in Fig. 11 and Fig. 12, that is, the change in apparent g-factor by varying the density of specimens is due to the change in the magnitude of internal field, while the true g-value remain constant, and the relation between the magnetic field at resonance maximum and the employed microwave frequency is always kept in the relation expressed by the equation (1).

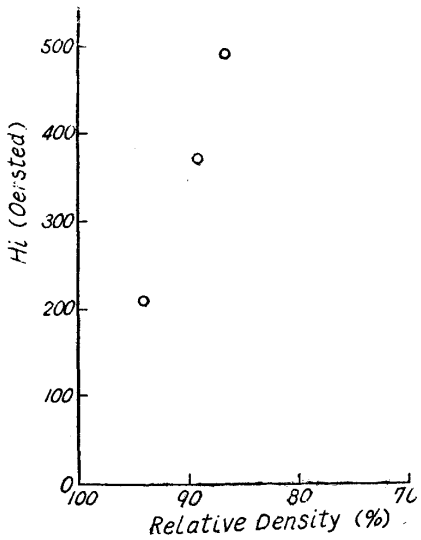

Fig. 13. H_i of nickel ferrite as a function of density.

The internal field which was deduced from equation (1) using the data at three frequencies were plotted in Fig. 13 and Fig. 14 as a function of relative density. Though it cannot be confirmed from the present result becuause of the lack of satisfactory extrapolation, whether the value of H_i at the specimen of 100% density reach zero or still show some value of scores of oersteds, but the decreasing inclination of internal field with increasing density suggests that H_i must be very small if an extremely dense specimen is used.

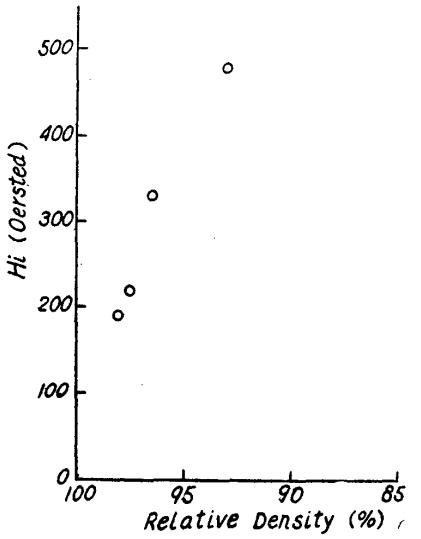

Fig. 14. H_i of manganese ferrite as a function of density.

Line width was also found to depend on the specimen's density as seen in Fig. 11 and Fig. 12, and the curves show that the line width of very dense specimen is about 400 oersteds or so for both ferrites.

Summary

The variation of g-factors with composition were found to be in agreement with the theory of Tuya-Wangsness in Ni–Zn, Mn–Zn binary ferrites and nickel ferrite aluminates, but in $NiFe_{2-x}Al_xO_4$ the results at $x > 0.72$ could not be explained by the theory.

The frequency dependence of apparent g-factor were found to be mainly due to the specimen's porosity.

Notwithstanding the change of apparent g-factor with varying density, the consideration of the internal field in the resonance condition to determine the frequency independent g-factor could be applied to the experiment on the specimens of various densities except for the specimen having too much porosity.

In conclusion, I should like to express my sincere thanks for the cooperation of Dr. Y. Torizuka during the course of this work.